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Mechanisms of emission stimulation in nanoparticles doped with rare earth and transition metal ions

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Abstract : In this work arguments are presented that phosphors of nanosizes may emit light more efficiently than conventional phosphor materials and thus can be applied in practical optoelectronic devices.

1. Introduction :

Phosphor materials doped with rare earth (RE) (or transition metal (TM)) ions are presently used in compact fluorescence lamps (CFLs) and GaN-based white light emitting diodes (w-LEDs). They convert light from UV (in CFLs) or blue-violet (in w-LEDs) to a visible light. Perspectives of application of nanosize phosphors in the CFLs and w-LEDs devices are still disputed. Despite the fact that it is often claimed that large surface-to-volume ratio of nanoparticles (NPs) will never allow for efficient light emission [1], some observations indicate that going to nanosize can be advantageous [2]. For example, Rayleigh scattering, which decreases in proportion to the sixth power of particle size [1], is noticeably reduced for NPs embedded in some resins, which allows obtaining transparent films for e.g. w-LED applications [3]. In this paper I discuss further arguments that a nanometer size of phosphor materials may help to achieve a higher light output. Mechanisms of emission stimulation in doped NPs are discussed.

2. Results and Discussion :

2.1 Size dependence :

The crucial question remains if there is a positive correlation between small size of NPs and their photoluminescence (PL) efficiency. Such correlation was observed by us for Pr^{3+} and Tb^{3+} doped ZrO_2 NPs, with their size regulated by a post-growth annealing [4]. By varying the annealing temperature from a room temperature up to 900 °C we could obtain ZrO_2 particles varying in size from 10 nm (in as-grown samples) to 100 nm (in powders annealed at 900 °C). We observed (see Fig. 1) decrease of the PL intensity in the largest NPs, mostly due to a decrease in intensity of the red $^1\text{D}_2\text{-}^3\text{H}_4$ 4f-4f emission. Similar dependence we also observed for Tb^{3+} 4f-4f PL. This observation contradicts some previous reports for e.g. for a red $\text{CaTiO}_3\text{:Pr}^{3+}$ nanophosphor [5], which when annealed at temperature above 600 °C, which resulted in larger NPs, showed an increased PL efficiency. It thus remains an open question why in some cases smaller NPs emit more efficiently and not in other cases. This point must be cleared out and will determine chances of NPs application.

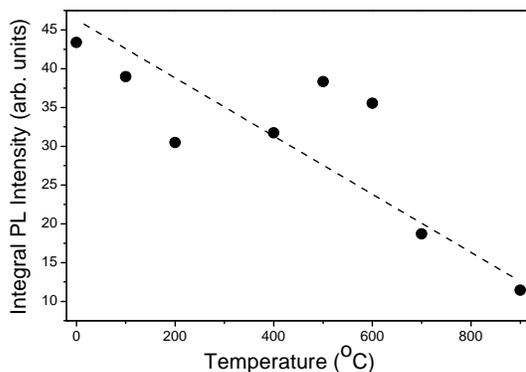


Figure 1: Dependence of the integrated PL intensity of Pr^{3+} ions in ZrO_2 measured for the sample with 1% Pr fraction for as grown sample (of 10 nm size) and annealed at temperatures up to 900 °C (NPs size increases to 100 nm).

2.2 Enhanced rate of radiative decay processes in nanoparticles :

Interest in NPs as phosphor materials started with the work of Bhargava and coworkers, who reported 3.7 and 20.5 ns PL decay time of the 4T_1 to 6A_1 transition of Mn^{2+} ions in ZnMnS NPs instead of ms one [6]. Such lifetime shortening was observed together with an increase in emission efficiency, i.e., the effect (in the authors opinion) could not be related to enhanced rate of a nonradiative decay [6]. Even though the observation (ns PL decay turned out to be accompanied by a „normal” one in ms) and the proposed model of quantum confined atom (QCA) turned out to be wrong, many of the following works confirmed the appearance of ultra-short (ps-ns) and short (ns- μs) components of the PL decay in TM/RE doped NPs (see [7-9] and references given there), which were observed together with the slow (μs -ms) ones. PL, electron spin resonance and optically detected magnetic resonance investigations performed by us proved that the ultra-fast component of the PL decay is due to impurity-free carriers interactions, which are very enhanced in NPs [7-9].

In all the systems studied by us a multi-component PL decay was observed, which often can be related to the competition of nonradiative recombination transitions [10]. Explanation of a multi-component PL decay may also come from the work of Dicke [11] and recent investigations of self-assembled quantum dots (QDs) [12]. A spontaneous emission of diluted NPs or QDs must include their interaction with a radiation field, resulting in a cooperative radiation - a super radiance [11]. Indications of a super radiance in RE doped NPs were deduced by us from confocal microscopy investigations of PL kinetics of various RE doped oxide NPs diluted in a glycol (see for details [13] for Gd_2O_3). We observed that the fast ns component of the PL decay comes from regions of NPs accumulations, characterized also by a brighter light emission.

Super radiance is only expected at initial stages of the PL decay, resulting in the appearance of the so-called fast components of the PL decay. When concentration of excited ions drops, emission changes to a “normal” PL, with PL decay as expected for a given intra-shell transition. This explains why a multi-component PL decay can be observed, with both fast and short PL components. Unfortunately, similar multi-component PL decay may indicate efficient nonradiative processes [10], intra-ion excitation migration, etc. Thus the observation of multi-component decay is not sufficient for a positive proof of a super radiance. However, in all the cases studied by us we observed that brighter emission comes from an ensemble of NPs, and that they show shorter components of the PL decay time, which agrees with the predictions of the super radiance mechanism. These results are thus strong indication of a super radiance mechanism.

The important question remains why the super radiance mechanism should be enhanced in the case of NPs. One possibility is that TM/RE ions are excited more efficiently in such host materials. In fact, we observed that such possibility may occur in NPs. PL excitation (PLE) spectra measured by us for terbium doped ZnS and for ZrO_2 NPs [14] indicate that an efficient 4f-4f intra-shell PL of Tb^{3+} is induced upon 4f-5d excitation of Tb^{3+} at the energy above a band gap energy of a host material. This suggests that in NPs RE ions may decorate surface or surface-close areas of NPs allowing more

efficient their excitation, by allowing 4f-5d excitation channel, even when its energy is above a band gap energy of a given host material. Moreover, we observed that the 4T_1 to 6A_1 intra-shell PL of Mn^{2+} ions in ZnS NPs can be efficiently pumped under band - to - band excitation, which was not observed for „bulk-like” ZnMnS samples [14]. We proposed that enhanced host to Mn^{2+} energy pumping is related to confinement enhanced Mn-free carrier interactions, which, as written above, is also responsible for the appearance of an ultra-short component of the PL decay.

3. Summary and Conclusions :

Our investigations indicate that the intra-shell emission of TM and RE ions can in some cases and for some host materials be significantly enhanced in NPs. We postulate an important role of super radiance processes.

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